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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C07C 37/00, 37/16, C08G 67/02	A1	(11) International Publication Number: WO 94/14739 (43) International Publication Date: 7 July 1994 (07.07.94)
(21) International Application Number: PCT/US93/12426 (22) International Filing Date: 20 December 1993 (20.12.93) (30) Priority Data: 07/997,982 28 December 1992 (28.12.92) US (71) Applicant: CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventor: CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US). (74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).		(81) Designated States: AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR THE PREPARATION OF POLYISOBUTYL HYDROXYAROMATICS (57) Abstract A process for the preparation of a polyisobutyl hydroxyaromatic compound which comprises alkylating a hydroxyaromatic compound in the presence of an acidic alkylation catalyst with a polyisobutene having a number average molecular weight in the range of about 300 to 5,000 and wherein the polyisobutene contains at least about 70 % of a methylvinylidene isomer.		

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01 PROCESS FOR THE PREPARATION OF POLYISOBUTYL HYDROXYAROMATICS

02

03

BACKGROUND OF THE INVENTION

04

05 This invention relates to a process for the preparation of
06 polyisobutyl hydroxyaromatics. More particularly, this
07 invention relates to a process for the preparation of
08 polyisobutyl hydroxyaromatics which comprises alkylating a
09 hydroxyaromatic compound with a polyisobutene having a
10 methylvinylidene isomer content of at least about 70%.

11

12 Alkylation of hydroxyaromatic compounds with polymeric
13 olefins using acidic catalysts to generate alkylphenols is
14 well known in the art. However, use of the acidic catalysts
15 required for the alkylation reaction gives rise to
16 concurrent polymer degradation and fragmentation of the
17 polymeric alkyl substituent on the hydroxyaromatic compound.
18 Known acidic alkylation catalysts have various fragmenting
19 effects depending on the size of the alkylating agent. Most
20 catalysts have little effect on olefin alkylating agents of
21 up to about 20 carbon atoms, that is, having a number
22 average molecular weight of up to about 280, but severe
23 fragmentation occurs where alkylating agents of higher
24 molecular weights are used. Polymeric alkylating agents are
25 usually derived from propylene or butene and those comprised
26 primarily of polybutene are the most susceptible to
27 fragmentation during the alkylation reaction. When
28 polybutenes having a number average molecular weight of 300
29 or greater are used, molecular weight degradation of either
30 the olefin polymer or the substituted alkyl group occurs.

31

32 British Patent No. 1,159,368 discloses that fragmentation of
33 both the alkylating agent and alkyl substituent can be
34 reduced but not eliminated by the use of certain specified

- 2 -

01 reaction conditions. These conditions include the use of
02 boron trifluoride-phenolate as the acidic catalyst and a
03 temperature range of 0°C to 65°C, with 0.1 to 1.1 moles of
04 boron trifluoride and 1 to 4 moles of phenol per mole of
05 mono-olefinic polymeric alkylating agent having a molecular
06 weight of 700 to 300,000. Under these conditions, the
07 fragmentation of polybutene can still only be restricted at
08 best to a level of about a 10% reduction of average
09 molecular weight.

10

11 U.S. Patent No. 4,238,628 to Cahill et al. discloses a
12 process to reduce the molecular weight degradation during
13 the alkylation of benzene, phenol and naphthol which
14 comprises alkylating the aromatic compound in the presence
15 of a boron trifluoride catalyst with a C₃ or higher olefin
16 polymer having terminal ethylene units.

17

18 According to the Cahill et al. process, the olefin polymer,
19 preferably polybutene, is first reacted with ethylene to
20 provide a polymer having terminal ethylene units. The
21 polymer having such terminal ethylene units is then reacted
22 with the aromatic compound under alkylating conditions.
23 Cahill et al. teach that the olefin structure of the
24 starting polybutene is predominantly the trisubstituted type
25 with only minor amounts of vinylidene and terminal vinyl
26 structures present.

27

28 Cahill et al. further teach that polyalkylphenols prepared
29 with the use of polybutene without terminal ethylene units
30 undergo molecular weight degradation due to the concurrent
31 depolymerization reaction. Although the process disclosed
32 in Cahill et al. results in a reduction in polymer
33 degradation, the yield of the desired alkylaromatic product

34

01 is not enhanced. In fact, the yield of alkylphenol reported
02 by Cahill et al. ranged from about 44% to 64%.

03

04 Accordingly, there exists a need in the art for a
05 hydroxyaromatic alkylation process which minimizes or
06 eliminates molecular weight degradation while maintaining a
07 high yield of the desired alkylaromatic product.

08

09

SUMMARY OF THE INVENTION

10

11 The present invention provides a novel process for the
12 preparation of a polyisobutyl hydroxyaromatic compound which
13 comprises alkylating a hydroxyaromatic compound in the
14 presence of an acidic alkylation catalyst with a
15 polyisobutene having a number average molecular weight in
16 the range of about 300 to 5,000 and wherein the
17 polyisobutene contains at least about 70% of a
18 methylvinylidene isomer.

19

20 Among other factors, the present invention is based on the
21 surprising discovery that hydroxyaromatic compounds can be
22 effectively alkylated with a high molecular weight
23 polyisobutene under acid-catalyzed reaction conditions in
24 significantly high yield, while minimizing or substantially
25 eliminating molecular weight degradation of the starting
26 polyisobutene and the resulting polyisobutyl
27 hydroxyaromatic, by employing a polyisobutene which contains
28 a methylvinylidene isomer content of at least about 70%.
29 Moreover, when the hydroxyaromatic compound is phenol, the
30 resulting polyisobutyl phenol exhibits a high degree of para
31 substitution, particularly when compared to alkylphenols
32 prepared from conventional polybutenes having a low methyl
33 vinylidene content.

34

DETAILED DESCRIPTION OF THE INVENTION

01

02

03 As noted above, the present invention provides polyisobutyl
04 hydroxyaromatic compounds by a process which comprises
05 alkylating a hydroxyaromatic compound in the presence of an
06 acidic alkylation catalyst with a polyisobutene having a
07 number average molecular of about 300 to 5,000 and a
08 methylvinylidene isomer content of at least about 70%.

09

10 In general, the polyisobutyl substituent on the polyisobutyl
11 hydroxyaromatic compound will have a number average
12 molecular weight in the range of about 300 to 5,000,
13 preferably in the range of about 400 to 3,000, and more
14 preferably in the range of about 500 to 2,000.

15

16 The hydroxyaromatic compounds which may be alkylated in
17 accordance with the process of the present invention include
18 mononuclear monohydroxy and polyhydroxy aromatic
19 hydrocarbons having 1 to 4, and preferably 1 to 3, hydroxy
20 groups. Suitable hydroxyaromatic compounds include phenol,
21 catechol, resorcinol, hydroquinone, pyrogallol, and the
22 like. The preferred hydroxyaromatic compound is phenol.

23

24 The polyisobutene employed in the process of the present
25 invention is a polyisobutene having a high methylvinylidene
26 isomer content, that is, at least about 70%
27 methylvinylidene. Suitable high methylvinylidene
28 polyisobutenes include those prepared using boron
29 trifluoride catalysts. The preparation of such
30 polyisobutenes in which the methylvinylidene isomer
31 comprises a high percentage of the total olefin composition
32 is described in U.S. patent Nos. 4,152,499 and 4,605,808,
33 the disclosures of each of which are incorporated herein by
34 reference.

01 The polyisobutene contemplated for use in the present
02 invention will have a number average molecular weight in the
03 range of about 300 to 5,000, preferably in the range of
04 about 400 to 3,000, and more preferably in the range of
05 about 500 to 2,000.

06

07 Examples of suitable polyisobutenes having a high
08 methylvinylidene content include Ultravis 10, a
09 polyisobutene having a molecular weight of about 950 and a
10 methylvinylidene content of about 76%, and Ultravis 30, a
11 polyisobutene having a molecular weight of about 1300 and a
12 methylvinylidene content of about 74%, both available from
13 British Petroleum.

14

15 The catalyst employed in the process of the present
16 invention will generally be any of the well known acidic
17 alkylation catalysts. Typical acidic alkylation catalysts
18 include Lewis acids, trifluoromethanesulfonic acid, and
19 acidic molecular sieve catalysts. Suitable Lewis acids
20 include aluminum trichloride, boron trifluoride and boron
21 trifluoride complexes, such as boron trifluoride etherate,
22 boron trifluoride-phenol and boron trifluoride-phosphoric
23 acid. Typical molecular sieve type catalysts include
24 Amberlyst 36, available from Rohm and Haas, Philadelphia,
25 Pennsylvania. Preferred acidic alkylation catalysts include
26 trifluoromethanesulfonic acid, boron trifluoride and boron
27 trifluoride complexes. In general, the stronger acidic
28 alkylation catalysts will be employed with higher molecular
29 weight polyisobutenes.

30

31 Typically, the reaction temperature for the alkylation
32 reaction will be in the range of about 0°C to 100°C, and
33 preferably in the range of about 20°C to 60°C. The reaction

34

- 6 -

01 pressure will generally be atmospheric, although higher or
02 lower pressures may be employed.

03

04 The molar ratio of the hydroxyaromatic compound to
05 polyisobutene is normally in the range of about 1.2:1 to
06 5:1, and preferably will be in the range of about 2:1 to
07 3:1. In general, the number of equivalents of the acidic
08 alkylation catalyst per equivalent of polyisobutene will be
09 in the range of about 0.005:1 to 5:1, and preferably in the
10 range of about 0.05:1 to 0.6:1.

11

12 The alkylation reaction may be carried out neat or in the
13 presence of a solvent which is inert to the reaction of the
14 hydroxyaromatic compound and the polyisobutene. When
15 employed, a typical solvent is hexane.

16

17 The alkylation reaction will generally be carried out over a
18 period of about 2 to 48 hours, and preferably over a period
19 of about 3 to 20 hours. Upon completion of the reaction,
20 the desired polyisobutyl hydroxyaromatic compound is
21 isolated using conventional techniques.

22

23 The following examples are presented to illustrate specific
24 embodiments of this invention and are not to be construed in
25 any way as limiting the scope of the invention.

26

27

EXAMPLES

28

29

Example 1

30

31

Preparation of Polyisobutyl Phenol

32

33 To a flask equipped with a magnetic stirrer, reflux
34 condenser, thermometer, addition funnel and nitrogen inlet

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01 was added 203.2 grams of phenol. The phenol was warmed to
02 40°C and the heat source was removed. Then,
03 73.5 milliliters of boron trifluoride etherate was added
04 dropwise. 1040 grams of Ultravis 10 polyisobutene
05 (molecular weight 950, 76% methylvinylidene, available from
06 British Petroleum) was dissolved in 1,863 milliliters of
07 hexane. The polyisobutene was added to the reaction at a
08 rate to maintain the temperature between 22-27°C. The
09 reaction mixture was stirred for 16 hours at room
10 temperature. Then, 400 milliliters of concentrated ammonium
11 hydroxide was added followed by 2,000 milliliters of hexane.
12 The reaction mixture was washed with water (3 x 2,000
13 milliliters), dried over magnesium sulfate, filtered and the
14 solvents removed under vacuum to yield 1,056.5 grams of a
15 crude reaction product. The crude reaction product was
16 determined to contain 80% of the desired product by proton
17 NMR and chromatography on silica gel eluting with hexane,
18 followed by hexane: ethylacetate: ethanol (93:5:2).
19

20 Example 2

21
22 Various alkylation reactions were carried out in accordance
23 with the process of the present invention, using
24 polyisobutenes having a high methylvinylidene isomer
25 content. These reactions were compared with alkylation
26 reactions employing conventional polyisobutenes having only
27 minor amounts of methylvinylidene isomer present.
28
29 The polyisobutenes employed in the alkylation reactions
30 demonstrating the present invention were Ultravis 10
31 polybutene having a number average molecular weight of about
32 950 and a methylvinylidene isomer content of about 76% and
33 Ultravis 30 polyisobutene having a number average molecular
34 weight of about 1300 and a methylvinylidene isomer content

- 8 -

01 of about 74%, both of which are commercially available from
02 British Petroleum. The polyisobutenes employed for
03 comparison purposes were Parapol 950 polyisobutene having a
04 number average molecular weight of about 950 and a
05 methylvinylidene isomer content of about 2% and Parapol 1300
06 polyisobutene having a number average molecular weight of
07 about 1300 and a methylvinylidene isomer content of about
08 6%, both available from Exxon Chemical Company.

09
10 Each of the alkylation reactions were carried out using
11 2 equivalents of phenol as the hydroxyaromatic compound and
12 1 equivalent of polyisobutene. The reactions were carried
13 out over a period of about 15 hours.

14
15 The results are shown in Table 1. These results show that
16 the alkylation reactions of the present invention employing
17 high methylvinylidene polyisobutene provided the desired
18 polyisobutyl phenol in significantly higher yield than the
19 alkylation reactions employing conventional polyisobutene
20 having minor amounts of methylvinylidene. In addition, the
21 polyisobutyl phenols prepared in accordance with the present
22 invention exhibited minimal molecular weight degradation.
23 Moreover, the polyisobutyl phenols produced pursuant to the
24 present invention contained an average of about 70% to 100%
25 para-substitution. This compares to an average of about 0%
26 to 40% para-substitution for the polyisobutyl phenols
27 prepared with the conventional low vinylidene
28 polyisobutenes. Para-substituted polyisobutyl phenols are
29 preferable for a number of uses. For example, when
30 polyisobutyl phenols are employed as fuel additives,
31 para-substitution generally provides enhanced fuel additive
32 performance.

33

34

TABLE 1

Run No.	Polyisobutene	Acidic Catalyst	Mole Equiv. (Catalyst)	Temperature, °C	Yield	Mol. Wgt. (VPO) ^a	Mol. Wgt. (PMR) ^b
1	Parapol 950	CF ₃ SO ₃ H	.05 (0.8 wt. %)	Room Temp. ^c	61%	1069	1162
2	Ultravis 10	CF ₃ SO ₃ H	.05	Room Temp. ^c	91%	1114	1106
3	Parapol 950	BF ₃ • Et ₂ O	.55	Room Temp. ^c	15%	604	656
4	Ultravis 10	BF ₃ • Et ₂ O	.55	Room Temp. ^c	80%	1197	1218
5	Parapol 950	BF ₃ • H ₃ PO ₄	.55	Room Temp. ^c	11%	533	600
6	Ultravis 10	BF ₃ • H ₃ PO ₄	.55	Room Temp. ^c	83%		1162
7	Parapol 950	BF ₃ • phenol	.55	Room Temp. ^c	90%		656
8	Ultravis 10	BF ₃ • phenol	.05	45° C. ^d	82%		994
9	Parapol 1300	CF ₃ SO ₃ H	.05	Room Temp. ^c	14%	1088	994
10	Ultravis 30	CF ₃ SO ₃ H	.05	Room Temp. ^c	71%	1521	1386

a VPO = vapor pressure osmometry

b PMR = proton magnetic resonance

c Room Temperature was approximately 23°C.

d Reaction time was 5 hours.

PR3032

01 WHAT IS CLAIMED IS:

02

03 1. A process for the preparation of a polyisobutyl
04 hydroxyaromatic compound which comprises alkylating a
05 hydroxyaromatic compound in the presence of an acidic
06 alkylation catalyst with a polyisobutene having a
07 number average molecular weight in the range of about
08 300 to 5,000 and wherein the polyisobutene contains at
09 least about 70% of a methylvinylidene isomer.

10

11 2. The process according to Claim 1, wherein the
12 hydroxyaromatic compound is phenol.

13

14 3. The process according to Claim 1, wherein the
15 polyisobutene has a number average molecular weight of
16 about 400 to 3,000.

17

18 4. The process according to Claim 3, wherein the
19 polyisobutene has a number average molecular weight of
20 about 500 to 2,000.

21

22 5. The process according to Claim 1, wherein the acidic
23 alkylation catalyst is selected from the group
24 consisting of a Lewis acid, trifluoromethane sulfonic
25 acid and an acidic molecular sieve.

26

27 6. The process according to Claim 5, wherein the acidic
28 alkylation catalyst is a Lewis acid.

29

30 7. The process according to Claim 6, wherein the Lewis
31 acid is boron trifluoride or a boron trifluoride
32 complex.

33

34

-11-

- 01 8. The process according to Claim 5, wherein the acidic
02 alkylation catalyst is trifluoromethane sulfonic acid.
03
- 04 9. The process according to Claim 1, wherein the
05 alkylation temperature is in the range of about 0° to
06 100°C.
07
- 08 10. The process according to Claim 9, wherein the
09 alkylation temperature is in the range of about 20° to
10 60°C.
11
- 12 11. The process according to Claim 1, wherein the molar
13 ratio of hydroxyaromatic compound to polyisobutene is
14 about 1.2:1 to 5:1.
15
- 16 12. The process according to Claim 11, wherein the molar
17 ratio of hydroxyaromatic compound to polyisobutene is
18 about 2:1 to 3:1.
19
- 20 13. The process according to Claim 1, wherein the number of
21 equivalents of catalyst per equivalent of polyisobutene
22 is about 0.005:1 to 5:1.
23
- 24 14. The process according to Claim 13, wherein the number
25 of equivalents of catalyst per equivalent of
26 polyisobutene is about 0.05:1 to 0.6:1.
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34

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/12426

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C07C 37/00, 37/16; C08G 67/02

US CL :528/392; 568/790, 792, 793

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US, A, 5,192,335 (CHERPECK) 09 MARCH 1993.	1-14
A	US, A, 4,605,808 (SAMSON) 12 AUGUST 1986.	1-14
A	US, A, 4,238,628 (CAHILL) 09 DECEMBER 1980.	1-14
A	US, A, 4,231,759 (UDELHOFEN) 04 NOVEMBER 1980.	1-14
A	US, A, 4,152,499 (BOERZEL) 01 MAY 1979.	1-14

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search

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Authorized officer

JOHN KIGHT, III

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/12426

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

C07C 2/34, 9/00, 37/00, 37/16; C08F 4/00, 4/14, 8/32, 10/00; C08G 67/02; C10L 1/16; C10M 105/02; 44/442, 450;
252/51.5A; 525/381; 526/237, 272, 348.7; 528/392; 568/790, 792, 793; 585/15, 511, 516, 525